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Application number : 200202027-9

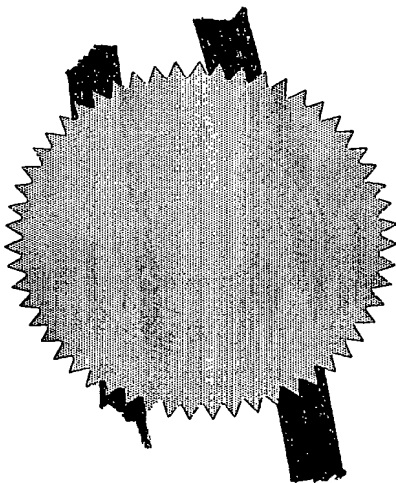
Applicant(s) : (A) INSTITUTE OF MATERIALS
RESEARCH AND ENGINEERING (B)
NATIONAL UNIVERSITY OF SINGAPORE

Title of Invention : METHOD FOR FORMING A MODIFIED
SEMICONDUCTOR HAVING A
PLURALITY OF BAND GAPS

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Tan Kar Leng (Miss)
Assistant Registrar
for Registrar of Patents
Singapore

10 April 2003 (10-04-2003)

**PRIORITY
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200202027-9
05 APR 2002

PATENTS FORM 1

Patents Act
(Cap. 221)
Patents Rules
Rule 19

INTELLECTUAL PROPERTY OFFICE OF SINGAPORE

REQUEST FOR THE GRANT OF A PATENT UNDER
SECTION 25

101101

* denotes mandatory fields

1. YOUR REFERENCE*

A1-1150 PK/rz

2. TITLE OF
INVENTION*METHOD FOR FORMING A MODIFIED SEMICONDUCTOR HAVING A
PLURALITY OF BAND GAPS

3. DETAILS OF APPLICANT(S)* (see note 3)

Number of applicant(s)

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200202027-9
05 APR 2002

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Further applicants are to be indicated on continuation sheet 1

4. DECLARATION OF PRIORITY (see note 5)

A. Country/country designated

File number

Filing Date

DD MM YYYY

B. Country/country designated

File number

Filing Date

DD MM YYYY

☐

Further details are to be indicated on continuation sheet 6

5. INVENTOR(S)* (see note 6)

A. The applicant(s) is/are the sole/joint inventor(s)

Yes

☐

No

☒

200202027-9
U 5 APR 2002

B. A statement on Patents Form 8 is/will be furnished

Yes

☒

No

☐

6. CLAIMING AN EARLIER FILING DATE UNDER (see note 7)

☐

section 20(3)

☐

section 26(6)

☐

section 47(4)

Patent application number

DD MM YYYY

Filing Date

Please mark with a cross in the relevant checkbox provided below
(Note: Only one checkbox may be crossed.)

☐

Proceedings under rule 27(1)(a)

DD MM YYYY

Date on which the earlier application was amended

☐

Proceedings under rule 27(1)(b)

7. SECTION 14(4)(C) REQUIREMENTS (see note 8)

Invention has been displayed at an international exhibition.

Yes

☐

No

☒

8. SECTION 114 REQUIREMENTS (see note 9)

The invention relates to and/or used a micro-organism deposited for the purposes of disclosure in accordance with section 114 with a depository authority under the Budapest Treaty.

Yes

☐

No

☒

9. CHECKLIST*

(A) The application consists of the following number of sheets

i.	Request	<input type="text" value="5"/>	Sheets
ii.	Description	<input type="text" value="18"/>	Sheets
iii.	Claim(s)	<input type="text" value="6"/>	Sheets
iv.	Drawing(s)	<input type="text" value="14"/>	Sheets
v.	Abstract (Note: The figure of the drawing, if any, should accompany the abstract)	<input type="text" value="1"/>	Sheets
Total number of sheets		<input type="text" value="44"/>	Sheets

(B) The application as filed is accompanied by:

☐

Priority document(s)

☐

Translation of priority document(s)

200202027-9
05 APR 2002

A

☒ Statement of inventorship
& right to grant

☐ International exhibition certificate

10. DETAILS OF AGENT (see notes 10, 11 and 12)

Name

Firm

ARTHUR LOKE BERNARD RADA & LEE

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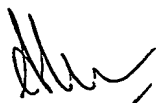
Postal Code

038989

12. NAME, SIGNATURE AND DECLARATION (WHERE APPROPRIATE) OF APPLICANT OR AGENT* (see note 12)
(Note: Please cross the box below where appropriate.)

☒ I, the undersigned, do hereby declare that I have been duly authorised to act as representative, for the purposes of this application, on behalf of the applicant(s) named in paragraph 3 herein.

PATSY KOH



Name and Signature

DD MM YYYY

05/04/2002

200202027-9
05 APR 2002

(A)

NOTES:

1. This form when completed, should be brought or sent to the Registry of Patents together with the rest of the application. Please note that the filing fee should be furnished within the period prescribed.
2. The relevant checkboxes as indicated in bold should be marked with a cross where applicable.
3. Enter the name and address of each applicant in the spaces provided in paragraph 3.
Where the applicant is an individual
 - Names of individuals should be indicated in full and the surname or family name should be underlined.
 - The address of each individual should also be furnished in the space provided.
 - The checkbox for "For individual applicant" should be marked with a cross.
Where the applicant is a body corporate
 - Bodies corporate should be designated by their corporate name and country of incorporation and, where appropriate, the state of incorporation within that country should be entered where provided.
 - The address of the body corporate should also be furnished in the space provided.
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Where the applicant is a partnership
 - The details of all partners must be provided. The name of each partner should be indicated in full and the surname or family name should be underlined.
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 - The checkbox for "For others" should be marked with a cross and the name and address of the partnership should be indicated in the box provided.
4. In the field for "Country", please refer to the standard list of country codes made available by the Registry of Patents and enter the country code corresponding to the country in question.
5. The declaration of priority in paragraph 4 should state the date of the previous filing, the country in which it was made, and indicate the file number, if available. Where the application relied upon in an International Application or a regional patent application e.g. European patent application, one of the countries designated in that application [being one falling under section 17 of the Patents Act] should be identified and the country should be entered in the space provided.
6. Where the applicant or applicants is/are the sole inventor or the joint inventors, paragraph 5 should be completed by marking with a cross the 'YES' checkbox in the declaration (A) and the 'NO' checkbox in the alternative statement (B). Where this is not the case, the 'NO' checkbox in declaration (A) should be marked with a cross and a statement will be required to be filed on Patents Form 8.
7. When an application is made by virtue of section 20(3), 26(6) or 47(4), the appropriate section should be identified in paragraph 6 and the number of the earlier application or any patent granted thereon identified. Applicants proceeding under section 26(6) should identify which provision in rule 27 they are proceeding under. If the applicants are proceeding under rule 27(1)(a), they should also indicate the date on which the earlier application was amended.
8. Where the applicant wishes an earlier disclosure of the invention by him at an International Exhibition to be disregarded in accordance with section 14(4)(c), then the 'YES' checkbox at paragraph 7 should be marked with a cross. Otherwise, the 'NO' checkbox should be marked with a cross.
9. Where in disclosing the invention the application refers to one or more micro-organisms deposited with a depository authority under the Budapest Treaty, then the 'YES' checkbox at paragraph 8 should be marked with a cross. Otherwise, the 'NO' checkbox should be marked with a cross. Attention is also drawn to the Fourth Schedule of the Patents Rules.
10. Where an agent is appointed, the fields for "DETAILS OF AGENT" and "ADDRESS FOR SERVICE IN SINGAPORE" should be completed and they should be the same as those found in the corresponding Patents Form 41. In the event where no agent is appointed, the field for "ADDRESS FOR SERVICE IN SINGAPORE" should be completed, leaving the field for "DETAILS OF AGENT" blank.
11. In the event where an individual is appointed as an agent, the sub-field "Name" under "DETAILS OF AGENT" must be completed by entering the full name of the individual. The sub-field "Firm" may be left blank. In the event where a partnership/body corporate is appointed as an agent, the sub-field "Firm" under "DETAILS OF AGENT" must be completed by entering the name of the partnership/body corporate. The sub-field "Name" may be left blank.
12. Attention is drawn to sections 104 and 105 of the Patents Act, rules 90 and 105 of the Patents Rules, and the Patents (Patent Agents) Rules 2001.
13. Applicants resident in Singapore are reminded that if the Registry of Patents considers that an application contains information the publication of which might be prejudicial to the defence of Singapore or the safety of the public, it may prohibit or restrict its publication or communication. Any person resident in Singapore and wishing to apply for patent protection in other countries must first obtain permission from the Singapore Registry of Patents unless they have already applied for a patent for the same invention in Singapore. In the latter case, no application should be made overseas until at least 2 months after the application has been filed in Singapore, and unless no directions had been issued under section 33 by the Registrar or such directions have been revoked. Attention is drawn to sections 33 and 34 of the Patents Act.
14. If the space provided in the patents form is not enough, the additional information should be entered in the relevant continuation sheet. Please note that the continuation sheets need not be filed with the Registry of Patents if they are not used.



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**METHOD FOR FORMING A MODIFIED SEMICONDUCTOR HAVING A
PLURALITY OF BAND GAPS**



G00002

Technical Field

5 The present invention relates to semiconductor heterostructures and, in particular, relates to a method for forming a modified semiconductor having a plurality of band gaps.

Background Art

10 Many optoelectronic devices consist of a quantum structure or quantum region embedded within a semiconductor heterostructure. These quantum regions may take the form of a quantum well, a superlattice, a quantum wire or a quantum dot. When manufacturing such semiconductor optoelectronic devices it is extremely important to control the optical band gap of the quantum structure.

15 The monolithic integration of optoelectronic components requires the production of a heterostructure which has different transition energy levels across different areas of its surface. Achieving these different transition energy levels is known as "band gap tuning".

 One known method of band gap tuning a semiconductor heterostructure is known as "impurity induced quantum well intermixing". This technique employs the diffusion of impurity atoms to enhance the quantum well intermixing. An example of this technique is described in US Patent No 5,815,522 (*Nagai*).

20

 This technique has the disadvantage that the diffusion of the impurities may alter the electrical properties of the semiconductor and deteriorate the optical quality of the device. For this reason, impurity induced intermixing is not quite suitable for the fabrication of active devices.

25

 Another known method is called "ion-implantation induced intermixing." According to this technique, the intermixing is enhanced by the defects generated during ion implantation. Alternatively, the intermixing may be enhanced by ions

implanted directly into the active region of the semiconductor. An example of this technique is described in US Patent No 6,027,989 (*Poole et al*).

One application of the technique is described in US Patent No 6,005,881 (*Ikoma*). That patent discloses a method of generating a semiconductor laser using ion implantation induced quantum well intermixing. The laser produced by that technique has a transparent output window structure which is suitable for high-powered operation.

However, one disadvantage of this method is that the ion implantation causes damage to the semiconductor heterostructure.

Another known method is called "impurity free vacancy enhanced disordering" (IFVD). According to this technique, a dielectric layer is deposited on top of the heterostructure in order to generate atomic vacancies at the interface of the dielectric layer and the semiconductor surface. These vacancies are generated at an elevated temperature. According to this technique the generated vacancies then diffuse into the heterostructure and thereby enhance the interdiffusion of atoms across the heterostructure.

The present inventors have developed a method for forming a modified semiconductor having a plurality of band gaps which overcomes or ameliorates at least some of the disadvantages of the prior art.

Disclosure of Invention

In a first aspect, the present invention provides a method for forming a modified semiconductor having a plurality of band gaps, the method comprising the steps of:

providing a semiconductor having a surface and a quantum region which emits photons in response to electrical or optical stimulation, the quantum region having an original band gap and being disposed under said surface;

applying a plurality of layers of a plurality of materials to a plurality of selected regions of said surface, said plurality of materials being adapted to cause, upon thermal annealing, a plurality of degrees of intermixing in a plurality

of portions of said quantum region disposed immediately below each of said selected regions of said surface; and

thermally annealing said plurality of layers to said surface such that said layers of said materials cause said plurality of degrees of intermixing in said plurality of portions of said quantum region thereby shifting the original band gaps
5 of said portions of said quantum region,

thereby forming a modified semiconductor which exhibits a plurality of different band gaps in said plurality of portions of said quantum region depending upon the positioning of said plurality of layers of said plurality of materials on the
10 surface immediately above the respective portions of said quantum region.

Preferably, the step of applying a plurality of layers of a plurality of materials to a plurality of selected regions of the surface comprises applying the plurality of layers in a dot and/or line pattern to the plurality of selected regions of the surface, each of the patterned layers having different dot and/or line densities,
15 and being adapted to cause, upon thermal annealing, a plurality of degrees of intermixing in a plurality of portions of the quantum region disposed immediately below each of the selected regions of the surface.

Preferably, the plurality of layers comprise between two and five layers and the plurality of materials comprise between two and five materials.

20 Preferably, at least one of said materials is selected from one of:

(a) SiO_2 ; or

(b) Si_xN_y , wherein x and y are integers greater than 0. More preferably, the step of applying the plurality of layers of the plurality of materials to the plurality of selected regions of the surface comprises applying at least one of
25 layers using one or more of the following techniques:

(a) plasma enhanced chemical vapor deposition (PECVD);

(b) E-beam evaporation; or

(c) the spin-on method.

Alternatively, at least one of the materials is selected from one of:

30 (a) LTInP (low temperature deposited InP); or

(b) LT(In)GaAs (low temperature deposited InGaAs or GaAs). More preferably, the step of applying the plurality of layers of the plurality of materials to the plurality of selected regions of the surface comprises applying at least one of the layers using one or more of the following techniques at a lower epitaxy temperature:

- (a) metal organic chemical vapor deposition (MOCVD); or
- (b) molecular beam epitaxy (MBE).

Preferably, the step of applying a plurality of layers of a plurality of materials to a plurality of selected regions of the surface comprises applying one or more of the layers in a pattern. More preferably, the step of applying one or more of the layers in a pattern comprises:

- (a) applying the layer to the selected region of the surface; and
- (b) patterning the layer using one or more of the following techniques:
 - (i) photolithography; or
 - (ii) electron-beam lithography.

Preferably, the step of applying one or more of the layers in a pattern comprises applying the one or more layers in one or more of:

- (a) a dot pattern comprising a plurality of dots separated by a plurality of spaces;
- (b) an inverse dot pattern comprising a plurality of inverse dots separated by a plurality of inverse spaces;
- (c) a line pattern comprising a plurality of lines separated by a plurality of spaces;
- (d) an inverse line pattern comprising a plurality of inverse lines separated by a plurality of inverse spaces; or
- (e) a planar pattern.

Preferably, the dots, inverse dots, lines and inverse lines have relatively uniform diameters within each pattern and wherein the spaces and inverse spaces are relatively uniform within each pattern. More preferably, the diameters

of the dots and lines is less than or equal to 2 μm . Even more preferably, the spaces and inverse spaces are less than or equal to 2 μm .

Preferably, the step of applying the plurality of layers of the plurality of materials to the plurality of selected regions of the surface comprises applying the
5 layers to a thickness ranging from 10 nm to 500 nm.

Preferably, the step of thermally annealing the heterostructure comprises rapidly thermally annealing the heterostructure by heating the heterostructure at temperatures ranging from 500 to 1000 $^{\circ}\text{C}$ for periods of time ranging from 1 to 1000 seconds.

10 Preferably, the semiconductor comprises:

- (a) a semiconductor substrate; and
- (b) a quantum region.

More preferably, the semiconductor substrate is made from either:

- (a) InP; or
- 15 (b) GaAs.

Preferably, the quantum region comprises one or more of:

- (a) a single quantum well structure;
- (b) a multiple quantum well structure;
- (c) a super lattice structure;
- 20 (d) a quantum wire structure; or
- (e) a quantum dot structure.

Preferably, the quantum well structure comprises of one or more of:

- (a) InGaAsP/InGaAsP;
- (b) InGaAsP/InP;
- 25 (c) InGaAs/InP;

- (d) GaAs/AlGaAs;
- (e) InGaAs/GaAs;
- (f) InGaAlAs/GaAs; or
- (g) InGaAsN/GaAs.

5

In a second aspect, the present invention provides a modified semiconductor having a plurality of band gaps, the semiconductor comprising:

- (a) a surface;
- (b) a quantum region which emits photons in response to electrical or optical stimulation, the quantum region having an original band gap and being disposed under said surface; and
- (c) a plurality of layers of a plurality of materials disposed on a plurality of selected regions of said surface, said plurality of materials being adapted to cause, upon thermal annealing, a plurality of degrees of intermixing in a plurality of portions of said quantum region disposed immediately below each of said selected regions of said surface;

wherein the plurality of layers are thermally annealed to said surface, and wherein said modified semiconductor exhibits a plurality of different band gaps in said plurality of portions of said quantum region according to the positioning of said plurality of layers of said plurality of materials on the surface immediately above the respective portions of said quantum region.

Preferably, the plurality of layers comprises a plurality of patterned layers disposed on the plurality of selected regions of the surface, each of the plurality of patterned layers comprising an array of dots and/or lines, each having different dot and/or line densities and being adapted to cause, upon thermal annealing, a plurality of degrees of intermixing in a plurality of portions of the quantum region disposed immediately below each of the selected regions of the surface.

In one form, the modified semiconductor takes the form of a laser.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

Preferred Embodiment

A preferred embodiment of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a flow chart illustrating the method of band gap tuning a semiconductor heterostructure according to the invention;

Figures 2A and 2B are schematic side views of a semiconductor heterostructure being band gap tuned according to a first preferred method;

Figures 3A to 3C are schematic side views of a semiconductor heterostructure being band gap tuned according to a second preferred method;

Figure 4 is a flow chart illustrating the third preferred method according to the invention;

Figures 5A to 5C are schematic plan views of dot and line patterns employed in the third preferred method of the present invention;

Figures 6A-6I are schematic side and plan views of a semiconductor heterostructure being band gap tuned according to the third preferred method;

Figure 7 is a graph of the photoluminescence spectra exhibited by a semiconductor heterostructure formed according to the second preferred method of the present invention;

Figure 8 is a graph illustrating the effect of annealing time on the blueshift of the photoluminescence peak wavelength of different layer materials;

Figure 9 is a graph illustrating the relationship between the coverage ratio and the wavelength of semiconductor heterostructures which have been band gap tuned according to the third preferred method;

Figure 10 shows the blueshift of the transaction energy versus the Si_xN_y coverage ratio of the samples used in the experiments whose results appear in the graph of Figure 9;

Figure 11 is a perspective schematic diagram of a monolithically integrated dual wavelength ridge waveguide laser manufactured according to the invention; and

Figure 12 is a plan view of a schematic diagram of a laser source with four different wavelengths, which could be manufactured according to the method of the present invention.

15

The present invention is a method of band gap tuning a semiconductor heterostructure. Figure 2A shows a side view of an example semiconductor heterostructure 1. As seen in that figure, the heterostructure includes a semiconductor substrate 2 having a surface 3 and a quantum region 4 embedded therein. In this preferred embodiment, the semiconductor substrate is made up of one or more layers of InP or GaAs.

The quantum region 4 may be a single quantum well structure, a multiple quantum well structure, a superlattice structure, a quantum wire structure, a quantum dot structure or their combinations. When the quantum region 4 takes the form of a quantum well structure, it may be made up of any one of:

25

- (a) InGaAsP/InGaAsP;
- (b) InGaAsP/InP;
- (c) InGaAs/InP;
- (d) GaAs/AlGaAs;

- (e) InGaAs/GaAs;
- (f) InGaAlAs/GaAs; or
- (g) InGaAsN/GaAs.

Figure 1 shows a simplified flow chart of the first and second preferred methods of the present invention. The first step involves applying 5 a layer of a first material to first selected regions of the semiconductor surface 3. This applying step is then repeated for as many additional layers of additional materials as required. The preferred embodiment includes two, three or four layers of different materials. Further layers are also envisaged.

10 The materials should be selected so that each of the different materials varies the intermixing efficiency of the quantum region 4 to different degrees. Some materials should enhance the intermixing efficiency of the quantum region whereas others should suppress the intermixing efficiency of the quantum region.

As shown in Figure 1, once the layers have been applied to the selected regions of the semiconductor surface 3, the next step involves annealing 7 the heterostructure. This annealing step will cause intermixing in the quantum region 4 and will produce a semiconductor heterostructure 1 with a surface 3 having particular regions which exhibit band gap shifts depending upon how many of layers of material they were covered by in the applying step 5. For example, if a region was only covered by a layer of the first material, it would exhibit a different band gap shift from another region of the surface which was only covered by a layer of the second material. In turn, a region which was covered by layers of both the first and second materials would exhibit a third degree of band gap shift.

Preferred embodiments of this method involving the application of two or three layers of material will now be described with reference to Figures 2A to 3C.

Turning to Figure 2A, the first preferred method involves applying 5 a layer of a first material 8 to a region marked "A" on the semiconductor surface 3. The next step shown in Figure 2B involves applying 6 a layer of a second material 9 to the regions marked "A" and "B" on the semiconductor surface 3.

The two materials 8,9 should be selected so that they vary the intermixing efficiency of the quantum region to different degrees. Some examples of appropriate layer materials are:

- (a) SiO_2 ;
- 5 (b) Si_xN_y wherein x and y are integers greater than zero;
- (c) LTInP (low temperature deposited InP); or
- (d) LT(In)GaAs (low temperature deposited InGaAs or GaAs).

The inventors have found the following combinations to work well as the first and second materials respectively; SiO_2 and Si_xN_y , LTInP and Si_xN_y ,
 10 LT(In)GaAs and Si_xN_y . A number of other combinations are also envisaged.

The layers of SiO_2 and Si_xN_y should be applied to the semiconductor surface 3 using any of the following techniques:

- (a) plasma enhanced chemical vapour deposition (PECVD);
- (b) E-beam evaporation; or
- 15 (c) the spin-on method.

The layers of LTInP and LT(In)GaAs should be deposited on the semiconductor surface at a lower epitaxy temperature by either of the following techniques:

- (a) metal organic chemical vapour deposition (MOCVD); or
- 20 (b) molecular beam epitaxy (MBE).

Returning to Figure 1, the next step involves thermally annealing the semiconductor heterostructure 1. This annealing step 7 involves rapidly thermally annealing the heterostructure at temperatures ranging from 500 to 1000°C for time periods ranging from 1 to 1000 seconds. Different band gap shifts can be
 25 achieved with different annealing temperatures and times. These variations are discussed below with reference to the graph of Figure 8.

This annealing causes intermixing in the quantum region 4 and results in different regions of the semiconductor surface 3 exhibiting different band gap shifts depending upon whether they were covered by a layer of the first material,

a layer of the second material, or a layer of each of the first and second materials. For example, the region marked "A" in Figure 2B would exhibit a band gap shift somewhere in between the band gap shifts usually exhibited by the first and second materials 8, 9, whereas the region marked "B" would exhibit a band gap shift corresponding to the usual band gap shift exhibited by the second material 9.

A second preferred method is illustrated in Figures 3A to 3C. The steps of applying 5 the layers of a first material 8 and a second material in Figures 3A and 3B are the same steps as described with reference to Figures 2A and 2B except 10 that the layer of the first material 8 is applied in the region marked "C" and the layer of the second material 9 is applied in the regions marked "C" and "D". The same numerals have been used to indicate corresponding integers.

Figure 3C shows the additional step of applying a layer of a third material 10 to a selected region (the regions marked "C", "D" and "E") of the surface 3. 15 The materials used in each of the three layers may be selected from the same group of materials suggested above in the two layer version. Alternative materials may also be selected, providing that the three materials are adapted to vary the intermixing efficiency of the quantum region to different degrees. This is so that different combinations of the layers produce different band gap shifts.

20 Once the semiconductor heterostructure 1 shown in Figure 3C is thermally annealed, the surface 3 of the semiconductor 1 will exhibit different band gap shifts at different regions of the surface depending upon the layers of first, second and third materials applied to that region.

By applying the different layers of material to different regions of the 25 surface, a variety of different band gap shifts can be achieved in different regions of the semiconductor surface.

The embodiments described so far have involved the steps of applying 5 two or more layers of materials and annealing 7 them to band gap tune a semiconductor heterostructure. The method illustrated in the flow chart of Figure 4 uses those same steps but adds the step of patterning 6 one or more of the 30 layers to produce a wider variety of possible band gap shifts.

Figures 5A to 5C are schematic plan views of dot and line patterns employed in this third preferred method of the present invention.

In Figure 5A a dot pattern is shown where the dots 11 each have a diameter of 1 μm . Each of the dots are separated from each other by 2 μm .

5 In Figure 5B a dot pattern is shown where the dots 11 each have a diameter of 1 μm . Each of the dots are separated from each other by 1 μm .

In Figure 5C a line pattern is shown in which each of the lines 12 have a diameter of 1 μm and are separated from one another by 2 μm .

10 The inventors have found that by applying the layers in these regular patterns, they can accurately control the surface coverage of particular materials and thereby control the band gap tuning. For example, in Figure 5A, the spaces between the dots represent 90% of the surface area, the spaces between the dots in Figure 5B represent 75% of the surface area and the spaces between the lines in Figure 5C represent 67% of the surface area.

15 The inventors have found favourable results by applying a layer of material and then patterning the layer into the dot or line arrays using photolithography or electron-beam lithography. In the preferred embodiment, the diameters and separations of the dots 11 and lines 12 are relatively uniform and range from less than 1 μm up to 2 μm . Alternative pattern styles, sizes and separations are also
20 envisaged including inverse dot patterns, inverse line patterns, planar patterns, lattice style patterns and the like.

Figure 6A to 6I are schematic side and plan views of a semiconductor heterostructure being band gap tuned according to the third preferred method which includes this patterning step.

25 As shown in Figure 6A, the method involves applying 5 a layer of a first material 8 to a semiconductor heterostructure 1 having a surface 3 and a quantum region 4.

As shown in Figure 6B, the next step involves removing part of the layer of first material from the surface 3 leaving a covered region marked "F" and an
30 uncovered region marked "G".

The next step, shown in the side view of Figure 6C, involves patterning 6 the layer of the first material 8. In this example, two types of dot pattern are used. Referring to the plan view of Figure 6D, the first pattern is applied to the area of the surface defined by the combination of the regions marked "F" and "H". This
5 first pattern is a dot pattern of 1 μm dots 11 separated from each other by spaces 13 of 1 μm . The second dot pattern applied to the area of the surface defined by the combination of the regions marked "F" and "J" is a pattern of 1 μm dots separated by distances of 2 μm .

Turning to Figure 6E, the next step involves applying a layer of a second
10 material 9 to the semiconductor surface 3. In this example, it can be seen that the second material fills the spaces 13 between the dots 11 of the first material in the region marked "F". The layer of the second material also covers the region of the surface marked "G".

Turning to Figure 6F, the next step involves patterning 6 the layer of the
15 second material 9. In this example, two different line patterns are used in the region marked "G" to produce a number of lines 12 of the second material 9. As shown in the plan view of Figure 6G, the first line pattern 17 is applied to the area of the surface defined by the combination of the regions marked "G" and "H". This is a line pattern of 1 μm lines 12 separated from one another by 2 μm
20 spaces 13. The second line pattern 18 formed in the area of the surface defined by the combination of the regions marked "G" and "J" is a line pattern consisting of 1 μm lines 12 separated from one another by 1 μm spaces 13.

Turning now to Figure 6H, the next step involves applying a layer of a third
25 material 10 to the surface 3 of the semiconductor 1. As shown in that figure, the layer of third material 3 fills the gaps 13 between the lines 12 of the second material 9 in the region marked "G".

The next step involves thermally annealing 7 the heterostructure to cause
intermixing in the quantum region thereby producing a semiconductor heterostructure with a surface having particular regions which exhibit different
30 band gap shifts depending on which combination of materials they were covered by.

Figure 6I shows the resultant semiconductor surface in plan view. Each of the four main regions of the semiconductor surface 3 (FH, FJ, GH and GJ) will exhibit different transition energy shifts depending up on the coverage ratio of each of the three materials.

5 Using this invention, a large variety of band gap shifts can be achieved by combining two, three, four or more layers of different materials and by applying them in different coverage ratios by patterning the layers in different ways. Figures 7 to 10 provides some specific examples of the different band gap shifts which can be achieved using different materials, different annealing processes
10 and different pattern coverage ratios.

Figure 7 shows a graph of the photoluminescence spectra exhibited by a semiconductor heterostructure tuned according to the method of the present invention. In this example used a layer of LTInP 15 was applied to a first region of the surface, a layer of SiO₂ 14 was applied to an adjacent region of the surface
15 and a layer SiN 16 was applied to another region of the surface. The surface of the heterostructure was a thin InGaAs capping layer. The semiconductor heterostructure was then rapidly thermally annealed at 750°C for 60 seconds. The X axis of Figure 7 represents the wavelength (in nanometres) and the Y axis represents the photoluminescent intensity exhibited by the quantum well
20 structure. It can be seen from Figure 7 that each of the different materials varied the intermixing efficiency of the quantum well structure to different degrees.

Figure 8 is a graph illustrating the effect of annealing time on the blueshift of the photoluminescence peak wavelength 9 of different layer materials. The X axis of Figure 8 represents the annealing time in seconds and the Y axis
25 represents the blueshift in nanometres. From these test results it can be seen that the blueshift of the photoluminescent peak energy for the SiO₂ covered sample 14 and the LTInP covered sample 15 increase as the annealing time increases. It can also be seen that a layer of LTInP will blueshift the band gap more than a layer of SiO₂. This graph also shows that the photoluminescent
30 peak energy for the Si_xN_y sample 16 remains substantially the same for the entire range of annealing times.

In the samples analysed the inventors applied Si_xN_y films with thicknesses ranges from 30 nm to 240 nm using plasma enhanced chemical vapour deposition (PECVD). The inventors found that the suppression effect, in terms of photoluminescent blueshift, was the same for all of these thicknesses of film.

5 These tests suggested that the material which blueshifts the band gap the least is Si_xN_y , the material which blueshifts the band gap the most is LTInP and the material which blueshifts the band gap to a medium degree is SiO_2 .

Turning now to Figure 9, this graph illustrates the effectiveness of the patterning step in band gap tuning a semiconductor heterostructure. In this

10 experiment a semiconductor heterostructure having a three quantum well structure consisting of InGaAsP/InP was used. Five sample semiconductors were covered by a layer of Si_xN_y and a layer of SiO_2 in different $\text{Si}_x\text{N}_y/\text{SiO}_2$ coverage ratios. The 0% coverage ratio indicates that the surface area was totally covered by SiO_2 . The 10% coverage ratio indicates that the surface area

15 was covered by 10% Si_xN_y and the 100% coverage ratio indicates that the surface area was entirely covered by Si_xN_y . The intermediate coverage ratios are self explanatory. This experiment indicated that the wavelengths exhibited by the quantum well could be accurately manipulated by varying the coverage ratios of the different layers.

20 It also indicated that the intermixing in the quantum wells was uniform since the photoluminescent spectra for samples with different $\text{Si}_x\text{N}_y/\text{SiO}_2$ coverage ratios had similar line widths.

Figure 10 shows the blueshift of transition energy versus the Si_xN_y coverage ratio of the samples used in the experiments shown in Figure 9. The X

25 axis of Figure 10 indicates the Si_xN_y coverage ratio expressed as a percentage of the surface area, the Y axis represents the energy shift in meV. This graph shows that the largest blueshift was exhibited by the sample that was fully covered with SiO_2 . The least shift was that exhibited by the sample having its surface fully covered by Si_xN_y . Three intermediate values were also shown.

30 Using this technique the inventors were able to achieve at least five different transition energies in different areas of a single semiconductor heterostructure using just two different materials and one thermal annealing step.

The inventors have found that the same technique may also be applied to a combination of Si_xN_y and LTInP or Si_xN_y and LT(In)GaAs but with a larger blueshift in the photoluminescent spectra for the same Si_xN_y coverage ratio. Other favourable results were found using a combination of SiO_2 and LTInP or SiO_2 and LT(In)GaAs because the materials vary the intermixing efficiency of the quantum region to different degrees.

To obtain a wider range of transition energy shifts when fabricating more complicated or large scale photonic integrated circuits, three or more layers of materials can be employed at the same time. By varying the coverage ratios of the various materials many more transition energy shifts can be achieved across the heterostructure.

One application example of the present invention is shown in Figure 11. That figure shows a perspective schematic diagram of a monolithically integrated dual wavelength ridge waveguide laser. The example shown is a graded index separate confinement heterojunction (GRINSCH) laser structure. The n-type substrate 21 may be a GaAs or InP semiconductor or the like. On top of the substrate 21 is a lower cladding layer 22 with n-type doping to $2 \times 10^{18} \text{ cm}^{-3}$. The laser also includes an upper cladding layer 26 with p-type doping to $5 \times 10^{18} \text{ cm}^{-3}$. Between the lower and upper cladding layers lie the lower 23 and upper 25 confinement layers which sandwich the active region 24 which, in this example, is a quantum well structure. The laser also includes metal contacts 28, 29 for the electrodes.

By applying different layers of different materials to the surface of the semiconductor heterostructure in different patterns, a number of different regions, each exhibiting different wavelengths, can be achieved. In this example, the combination of two films, either SiO_2 and Si_xN_y or LTInP-LT(In)GaAs and Si_xN_y may be used to achieve wavelengths λ_1 , λ_2 , λ_3 and λ_4 .

In this example gain region 16 has wavelength λ_1 and gain region 17 has wavelength λ_2 . The Y-junction coupler region 19 has a transition energy with wavelength λ_4 that is short enough to ensure that it is completely transparent to wavelengths λ_1 and λ_2 . The isolator 18 has a wavelength λ_3 that should be transparent to λ_1 but which absorbs wavelength λ_2 so that laser light from the

gain region 17 will not optically pump gain region 16 when only gain region 17 is electrically biased. In this way the four different band gap regions in the wafer can be used to produce a monolithically integrated dual wavelength ridge waveguide laser.

5 Figure 12 shows another example of an application of the present invention. That figure shows a plan view of a schematic diagram of a laser source with four different wavelengths, each of which have monolithically integrated modulators. In order to manufacture such a laser, the transition energy level of the heterostructure requires nine different values at nine different
10 regions across the surface. In order to achieve this result, three different encapsulating layers should be used with the patterning techniques illustrated with reference to Figures 6A to 6I.

As shown in Figure 12, the semiconductor heterostructure 1 should have the patterned layers applied to it in such a way as to produce active laser regions
15 30, 31, 32 and 33 having wavelengths λ_1 , λ_2 , λ_3 and λ_4 respectively. These active regions should be integrated with modulators 34, 35, 36 and 37 which each have transition energy levels which are slightly larger than those of the active regions to which they are connected. These modulators are integrated with Y-junction couplers 38 and 39 which are integrated with a further Y-junction coupler
20 19. These three Y-junction couplers combine to couple the four laser beams into the one output wave guide 20 which exhibits all four wavelengths. The Y-junction couplers should have transition energy levels and output wave guides which are larger than those of the active regions and the modulator regions in order to avoid absorption.

25 In order to form such a laser the heterostructure 1 needs to exhibit nine different transition energy levels, one for each of the four active regions, one for each of the four modulator regions and one further transition energy level for the three Y-junction couplers together. The present invention provides a method of readily achieving nine or more different transition energy levels in different areas
30 of a single heterostructure.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific

embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Claims:

1. A method for forming a modified semiconductor having a plurality of band gaps, the method comprising the steps of:

5 providing a semiconductor having a surface and a quantum region which emits photons in response to electrical or optical stimulation, the quantum region having an original band gap and being disposed under said surface;

10 applying a plurality of layers of a plurality of materials to a plurality of selected regions of said surface, said plurality of materials being adapted to cause, upon thermal annealing, a plurality of degrees of intermixing in a plurality of portions of said quantum region disposed immediately below each of said selected regions of said surface; and

15 thermally annealing said plurality of layers to said surface such that said layers of said materials cause said plurality of degrees of intermixing in said plurality of portions of said quantum region thereby shifting the original band gaps of said portions of said quantum region,

thereby forming a modified semiconductor which exhibits a plurality of different band gaps in said plurality of portions of said quantum region depending upon the positioning of said plurality of layers of said plurality of materials on the surface immediately above the respective portions of said quantum region.

20

2. A method according to claim 1 wherein said plurality of layers comprises between two and five layers and wherein said plurality of materials comprises between two and five materials.

25 3. A method according to claim 1 or claim 2 wherein at least one of said materials is selected from one of:

(a) SiO_2 ; or

(b) Si_xN_y , wherein x and y are integers greater than 0.

4. A method according to claim 3 wherein said step of applying said plurality of layers of said plurality of materials to said plurality of selected regions of said surface comprises applying at least one of layers using one or more of the following techniques:

- 5 (a) plasma enhanced chemical vapor deposition (PECVD);
(b) E-beam evaporation; or
(c) the spin-on method.

10 5. A method according to claim 1 or claim 2 wherein at least one of said materials is selected from one of:

- (a) LTInP (low temperature deposited InP); or
(b) LT(In)GaAs (low temperature deposited InGaAs or GaAs).

15 6. A method according to claim 5 wherein said step of applying said plurality of layers of said plurality of materials to said plurality of selected regions of said surface comprises applying at least one of said layers using one or more of the following techniques at a lower epitaxy temperature:

- (a) metal organic chemical vapor deposition (MOCVD); or
(b) molecular beam epitaxy (MBE).

20

7. A method according to any one of claims 1 to 6 wherein the step of applying a plurality of layers of a plurality of materials to a plurality of selected regions of said surface comprises applying one or more of said layers in a pattern.

25

8. A method according to claim 7 wherein said step of applying one or more of said layers in a pattern comprises:

- (a) applying said layer to said selected region of said surface; and
(b) patterning said layer using one or more of the following techniques:

- (i) photolithography; or
- (ii) electron-beam lithography.

5 9. A method according to claim 7 or claim 8 wherein said step of applying one or more of said layers in a pattern comprises applying said one or more layers in one or more of:

- (a) a dot pattern comprising a plurality of dots separated by a plurality of spaces;
- 10 (b) an inverse dot pattern comprising a plurality of inverse dots separated by a plurality of inverse spaces;
- (c) a line pattern comprising a plurality of lines separated by a plurality of spaces;
- (d) an inverse line pattern comprising a plurality of inverse lines separated by a plurality of inverse spaces; or
- 15 (e) a planar pattern.

10. A method according to claim 9 wherein said dots, inverse dots, lines and inverse lines have relatively uniform diameters within each pattern and wherein said spaces and inverse spaces are relatively uniform within each pattern.

20

11. A method according to claim 10 wherein said diameters of said dots and lines is less than or equal to 2 μm .

12. A method according to claim 10 or claim 11 wherein said spaces and
25 inverse spaces are less than or equal to 2 μm .

13. A method according to any one of the preceding claims wherein said step of applying said plurality of layers of said plurality of materials to said plurality of

selected regions of said surface comprises applying said layers to a thickness ranging from 10 nm to 500 nm.

14. A method according to any one of the preceding claims wherein said step
5 of thermally annealing said heterostructure comprises rapidly thermally annealing said heterostructure by heating said heterostructure at temperatures ranging from 500 to 1000 °C for periods of time ranging from 1 to 1000 seconds.

15. A method according to any one of the preceding claims wherein said
10 semiconductor comprises:

- (a) a semiconductor substrate; and
- (b) a quantum region.

16. A method according to claim 15 wherein said semiconductor substrate is
15 made from either:

- (a) InP; or
- (b) GaAs.

17. A method according to claim 15 or claim 16 wherein said quantum region
20 comprises one or more of:

- (a) a single quantum well structure;
- (b) a multiple quantum well structure;
- (c) a super lattice structure;
- (d) a quantum wire structure; or
- 25 (e) a quantum dot structure.

18. A method according to claim 17 wherein said quantum well structure comprises of one or more of:

- (a) InGaAsP/InGaAsP;
- (b) InGaAsP/InP;
- (c) InGaAs/InP;
- (d) GaAs/AlGaAs;
- 5 (e) InGaAs/GaAs;
- (f) InGaAlAs/GaAs; or
- (g) InGaAsN/GaAs.

19. A modified semiconductor having a plurality of band gaps and being
10 formed by the method as defined in any one of claims 1 to 18.

20. A modified semiconductor according to claim 19 forming a laser.

21. A modified semiconductor having a plurality of band gaps, the
15 semiconductor comprising:

- (a) a surface;
- (b) a quantum region which emits photons in response to electrical or optical stimulation, the quantum region having an original band gap and being disposed under said surface; and
- 20 (c) a plurality of layers of a plurality of materials disposed on a plurality of selected regions of said surface, said plurality of materials being adapted to cause, upon thermal annealing, a plurality of degrees of intermixing in a plurality of portions of said quantum region disposed immediately below each of said selected regions of said surface;

25 wherein the plurality of layers are thermally annealed to said surface,

and wherein said modified semiconductor exhibits a plurality of different band gaps in said plurality of portions of said quantum region according to the positioning of said plurality of layers of said plurality of materials on the surface immediately above the respective portions of said quantum region.

22. A method for forming a modified semiconductor having a plurality of band gaps substantially as described herein with reference to the examples and drawings.



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Abstract

"Method for Forming a Modified Semiconductor having a Plurality of Band Gaps"

5 A method for forming a modified semiconductor having a number of band gaps. The first step involves providing a semiconductor having a surface and a quantum region which emits photons in response to electrical or optical stimulation, the quantum region having an original band gap and being disposed under the surface. The next step involves applying a number of layers of a

10 number of materials to a number of selected regions of the surface, the materials being adapted to cause, upon thermal annealing, a number of different degrees of intermixing in a number of portions of the quantum region disposed immediately below each of the selected regions of the surface. The layers of

15 materials can be applied in a dot or line pattern, or both, to increase the plurality of band gap tuning. The next step involves thermally annealing the layers to the surface such that the layers cause a number of degrees of intermixing in the different portions of said quantum region thereby shifting the original band gaps of those portions. These steps result in a modified semiconductor which exhibits

20 a number of different band gaps in a number of portions of the quantum region depending upon the positioning of the layers of materials on the surface immediately above the respective portions of the quantum region.

[Figure 6F]



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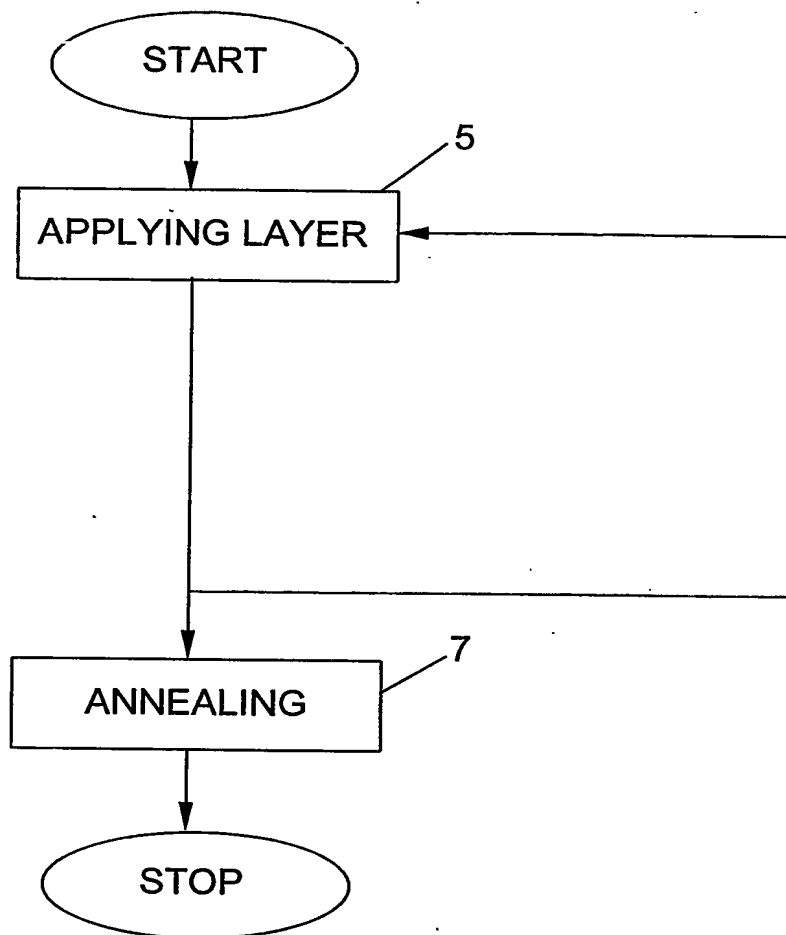


FIG. 1

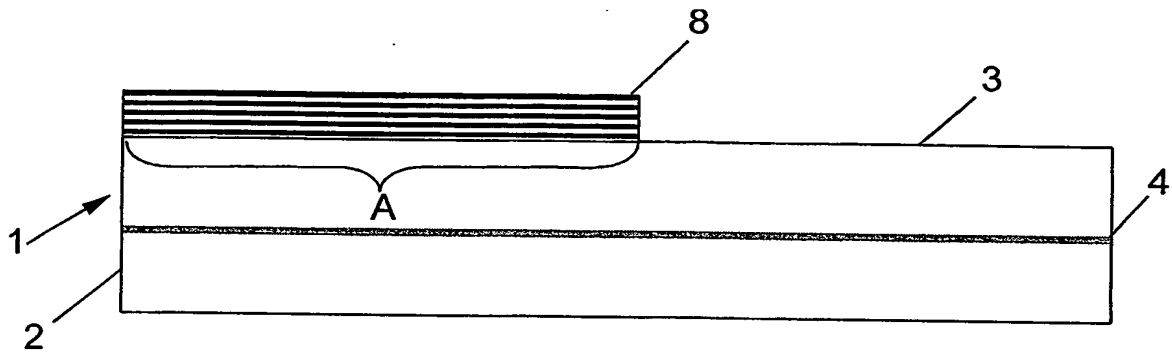


FIG. 2A

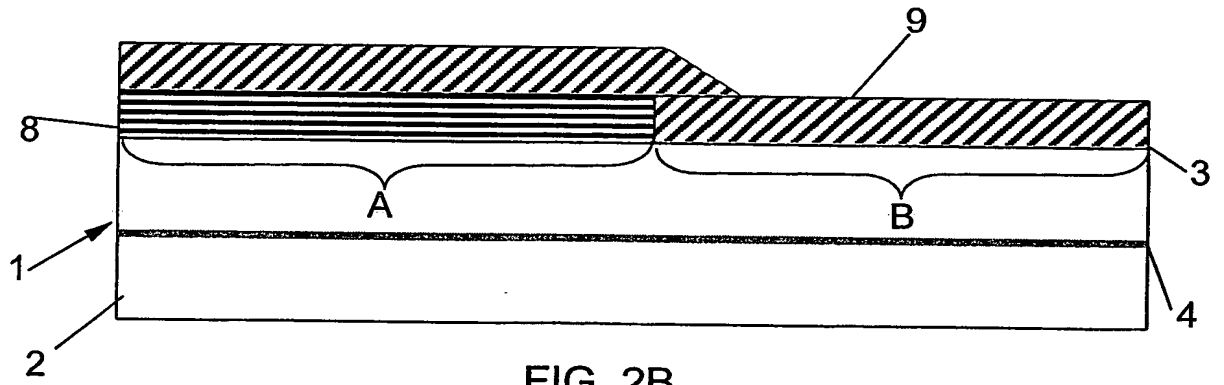


FIG. 2B

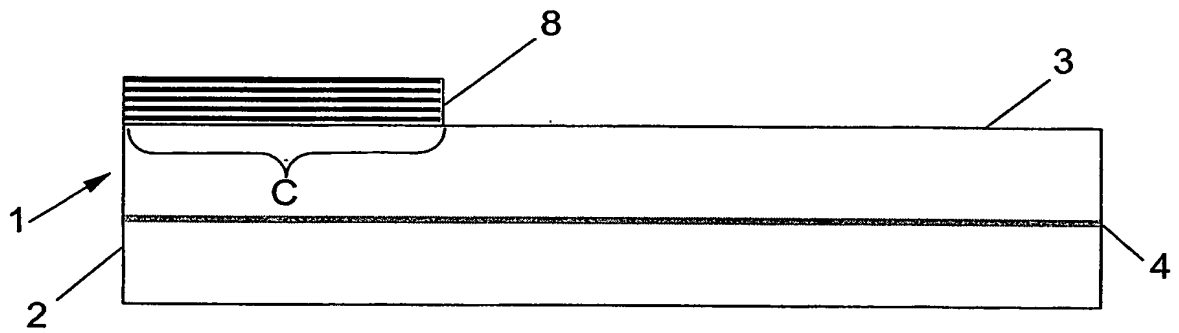


FIG. 3A

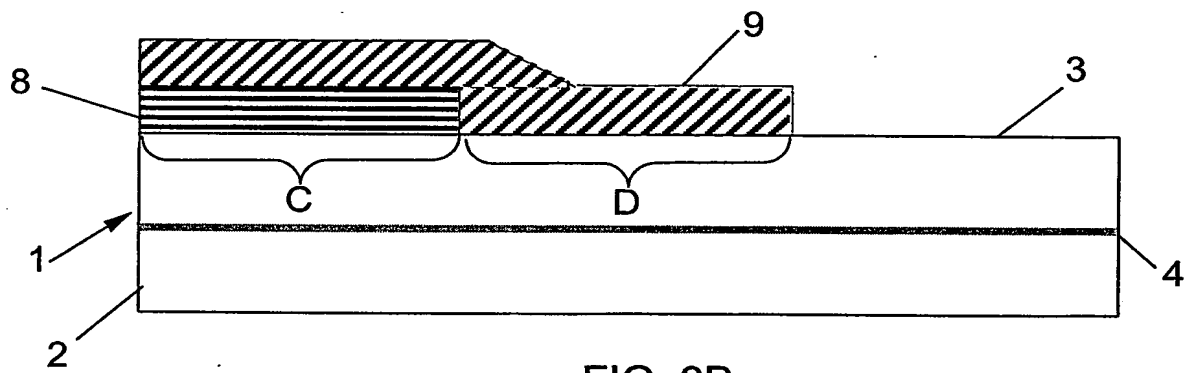


FIG. 3B

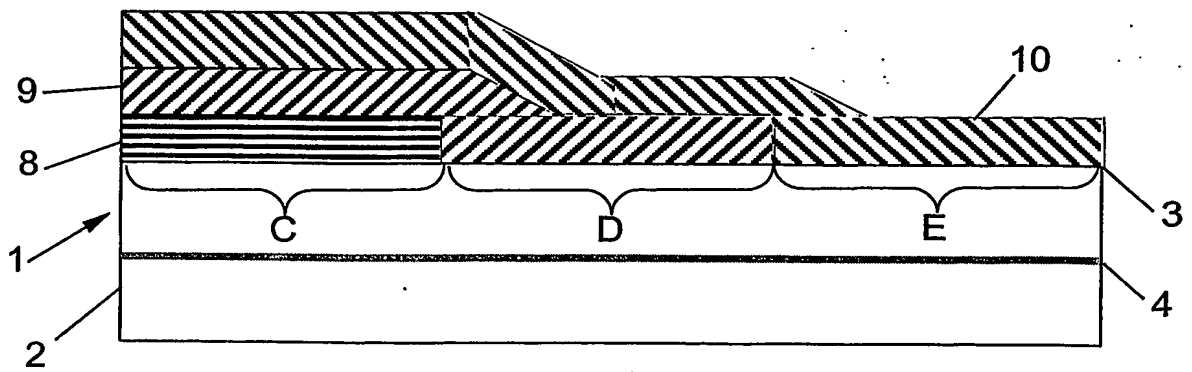


FIG. 3C

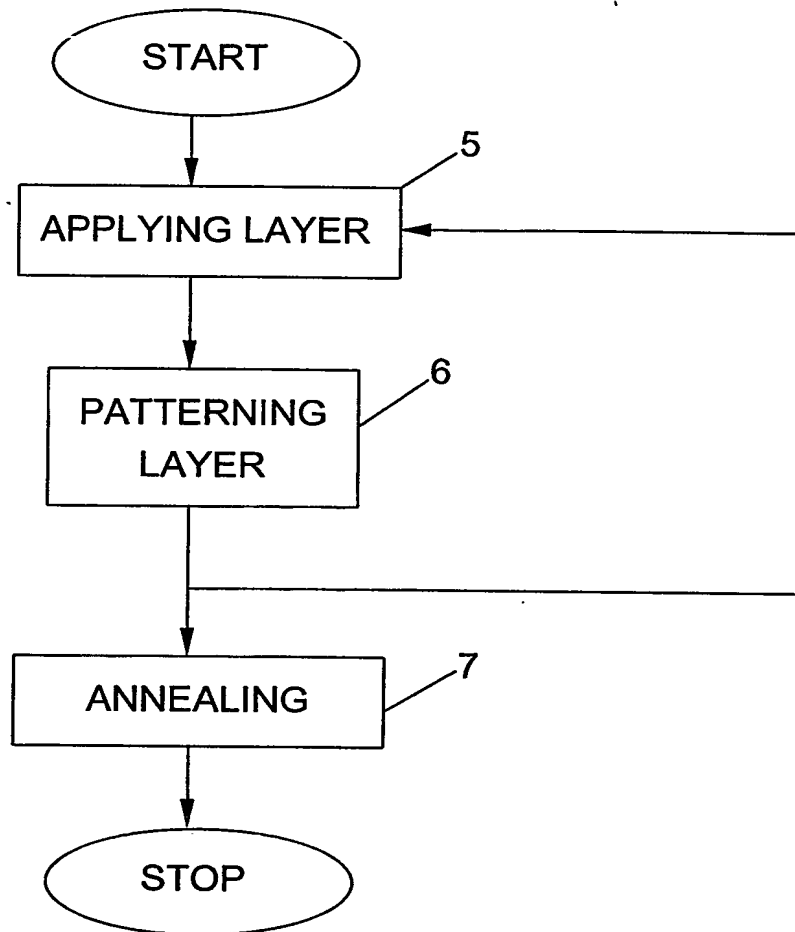


FIG. 4

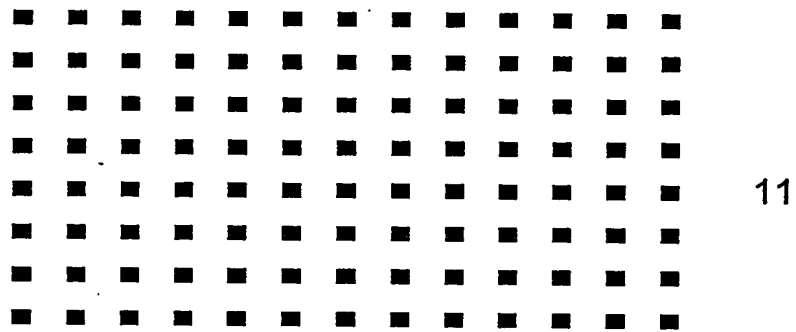


FIG. 5A

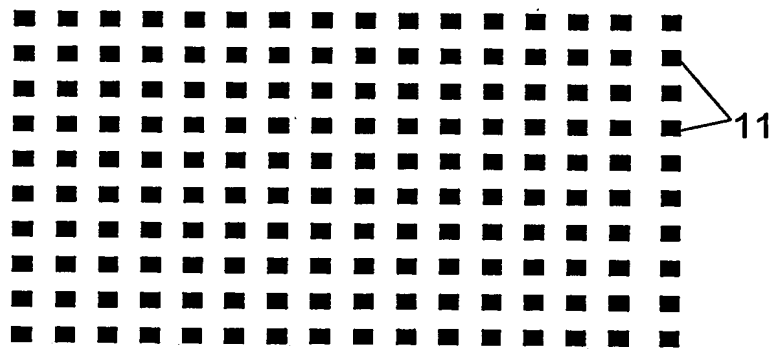


FIG. 5B

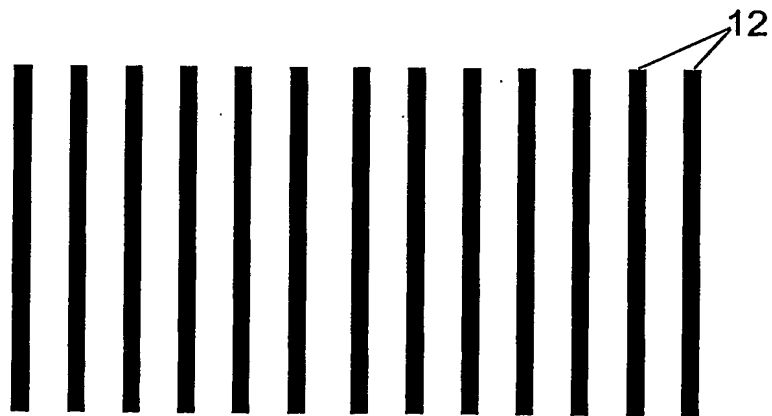


FIG. 5C

6/14

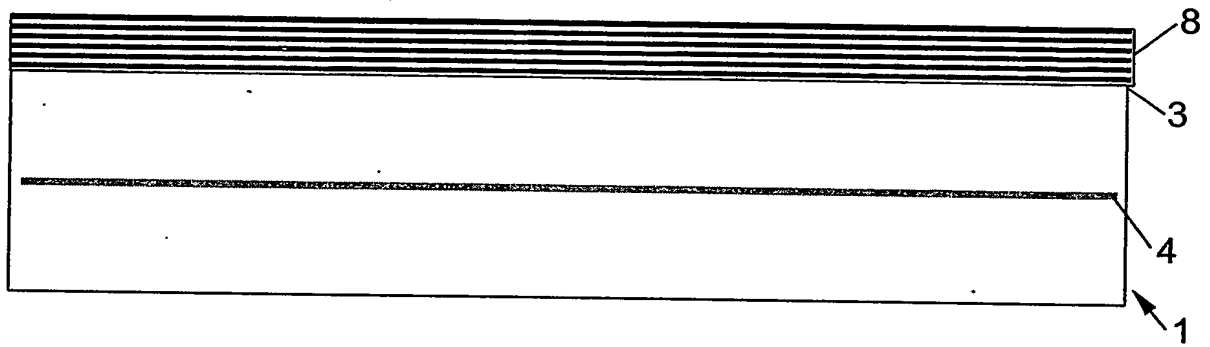


FIG. 6A

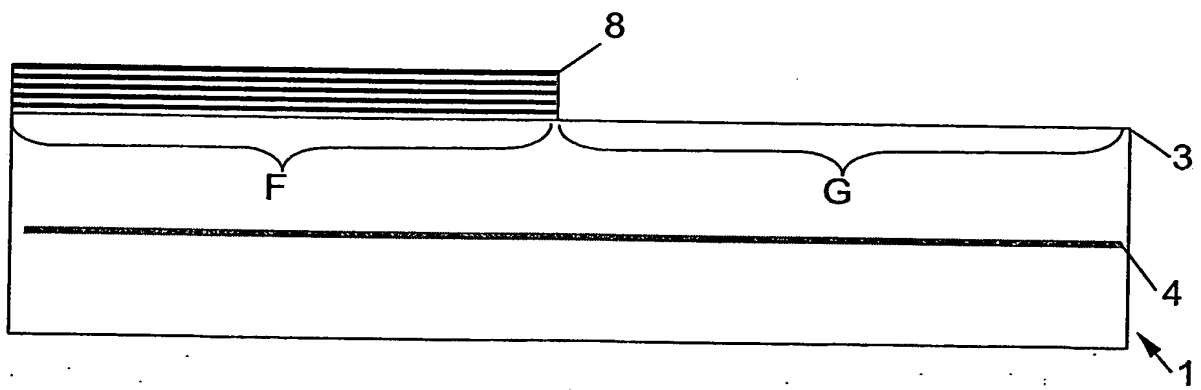


FIG. 6B

7/14

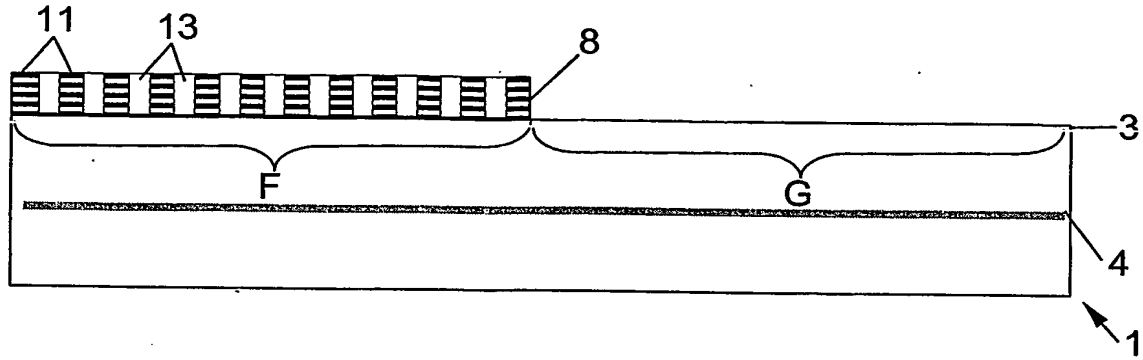


FIG. 6C

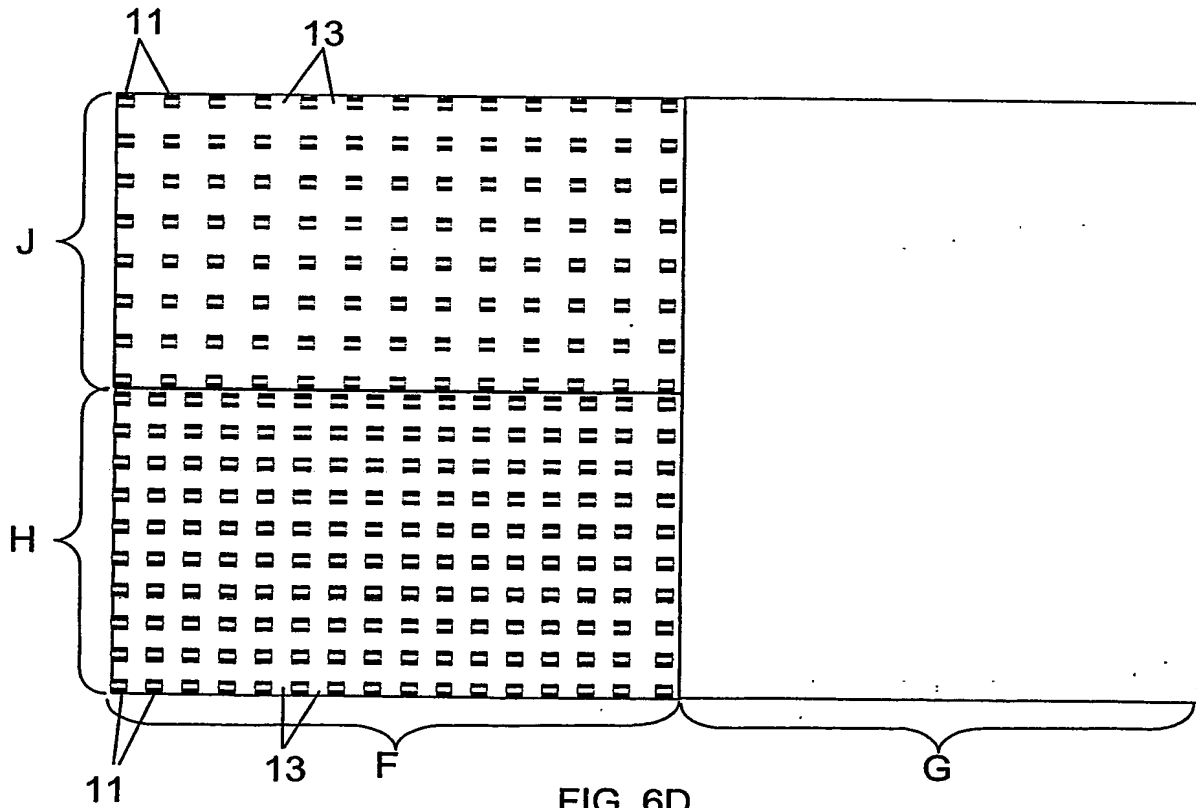


FIG. 6D

8/14

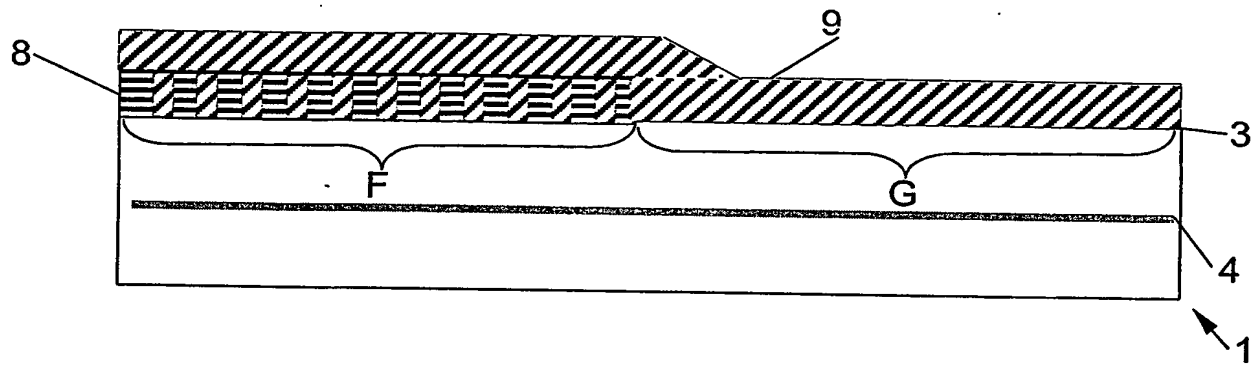


FIG. 6E

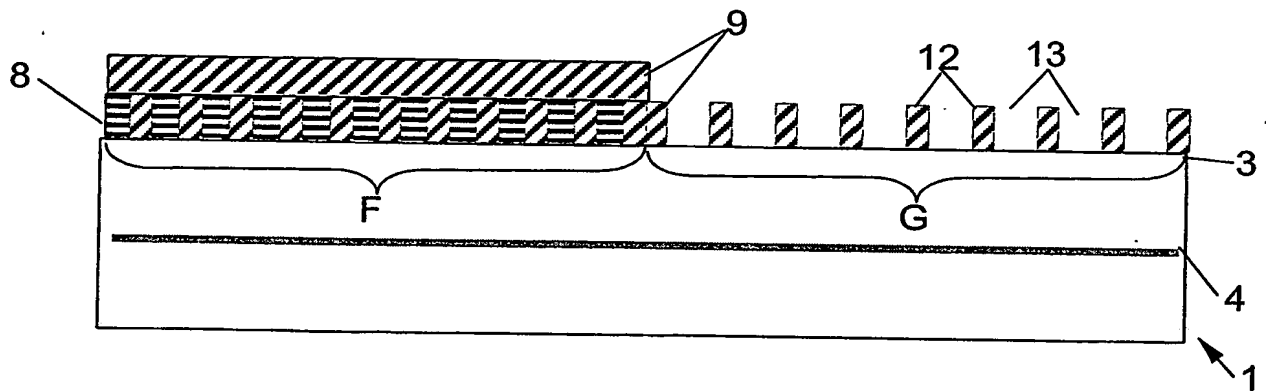


FIG. 6F

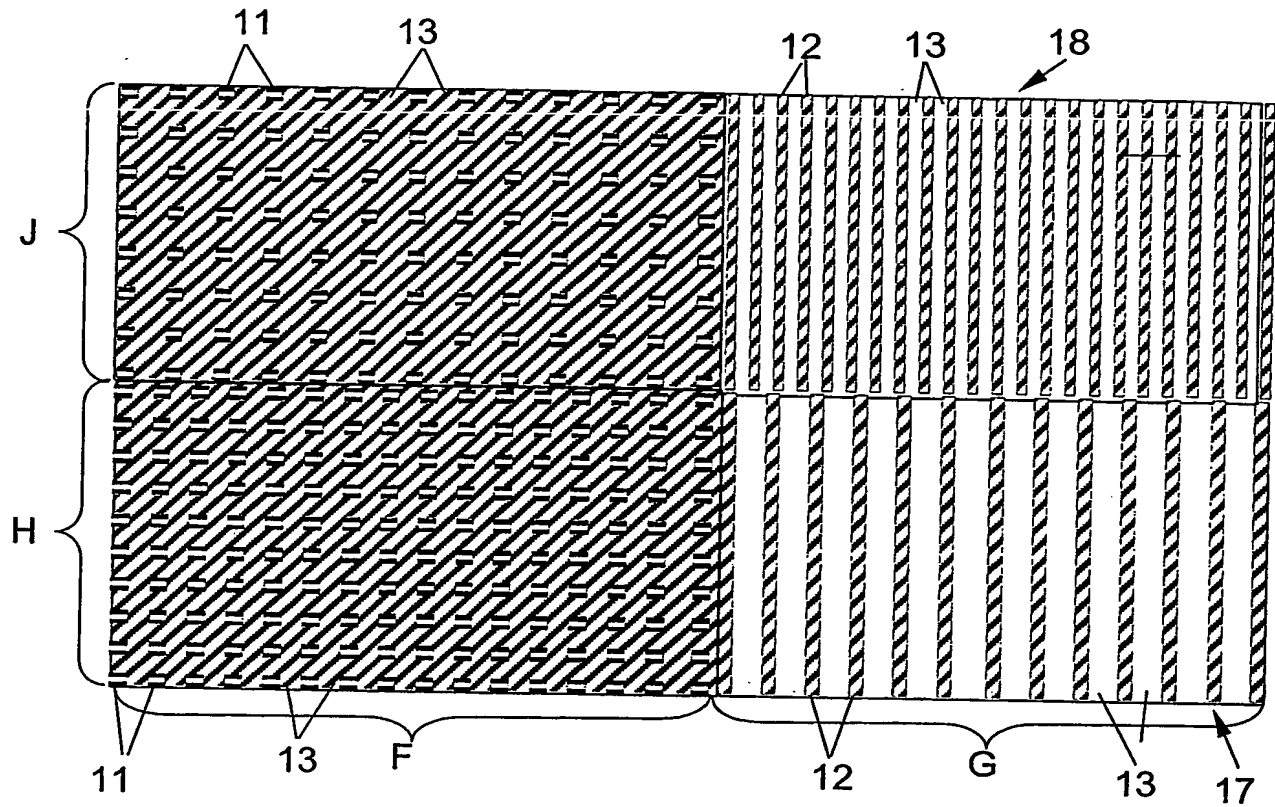


FIG. 6G

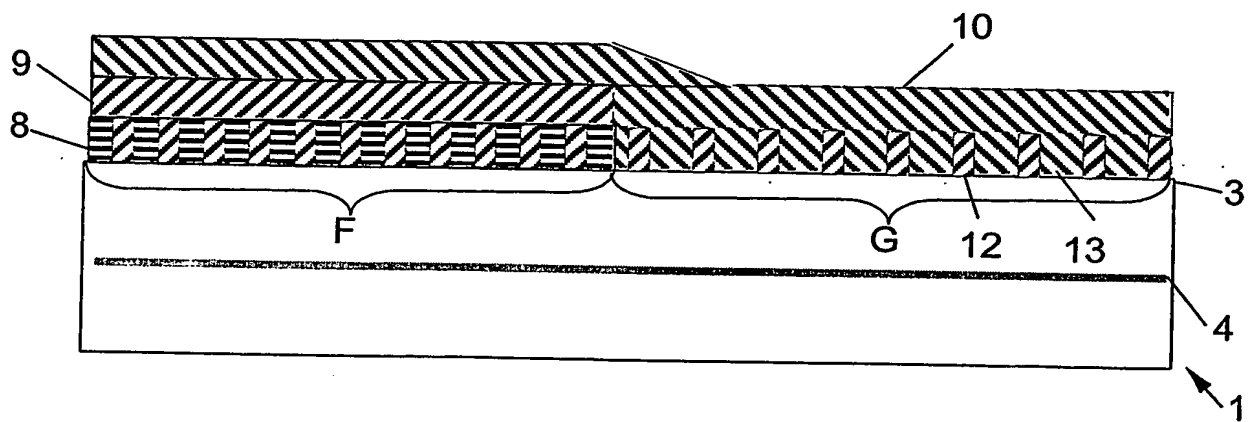


FIG. 6H

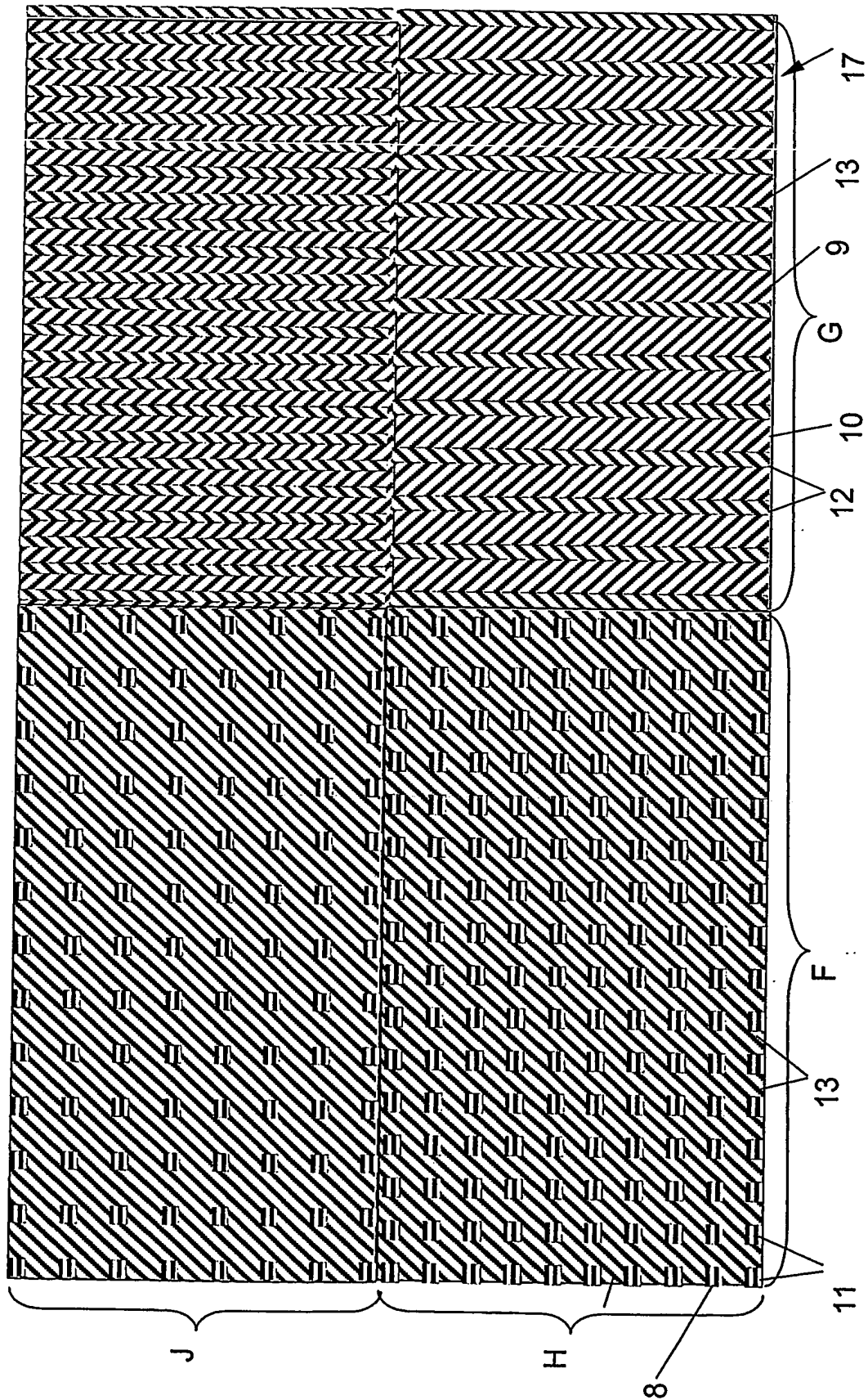


FIG. 6I

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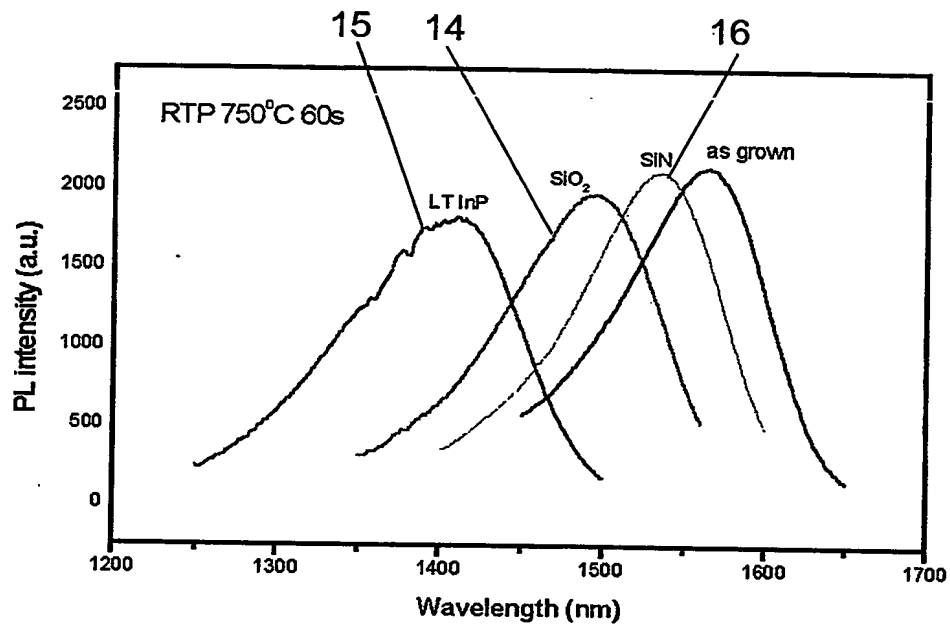


FIG. 7

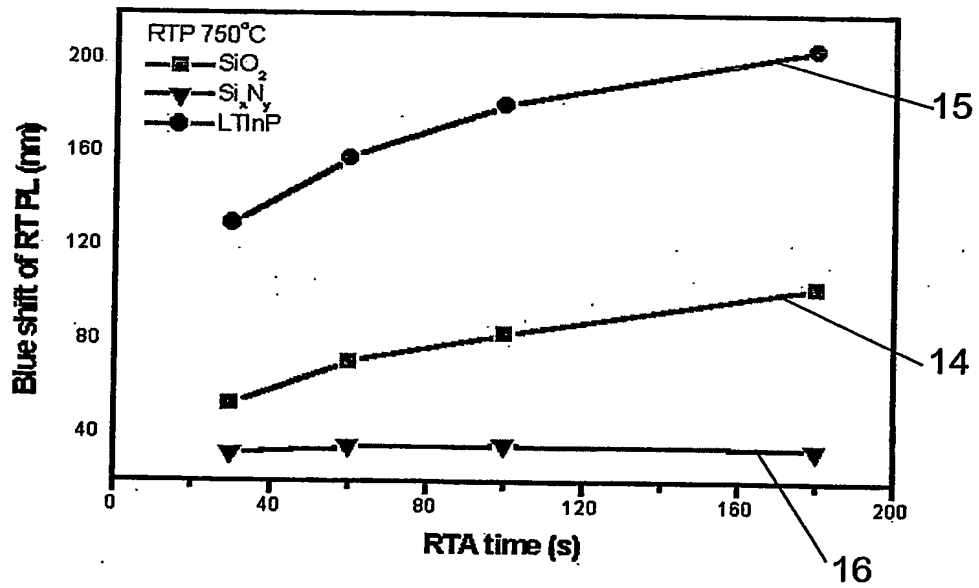


FIG. 8

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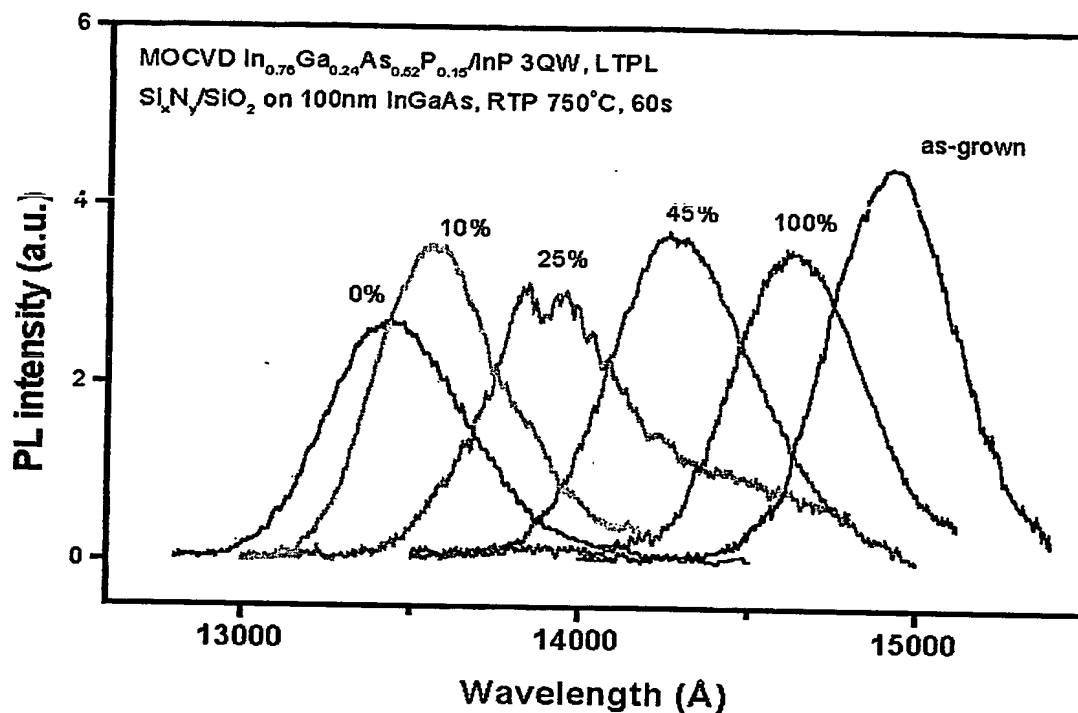


FIG. 9

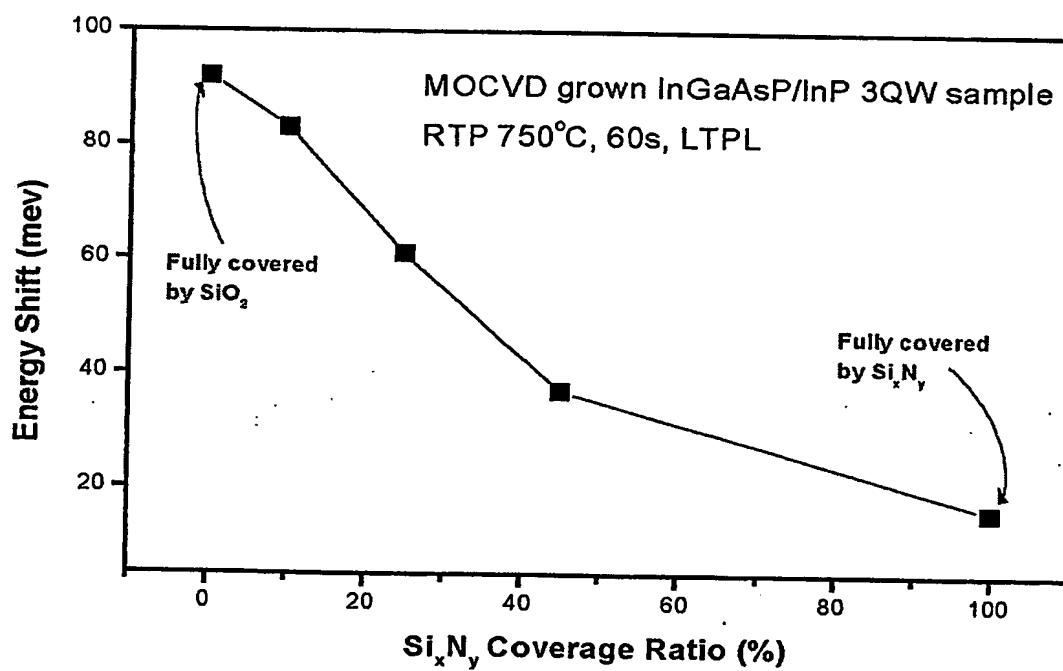


FIG. 10

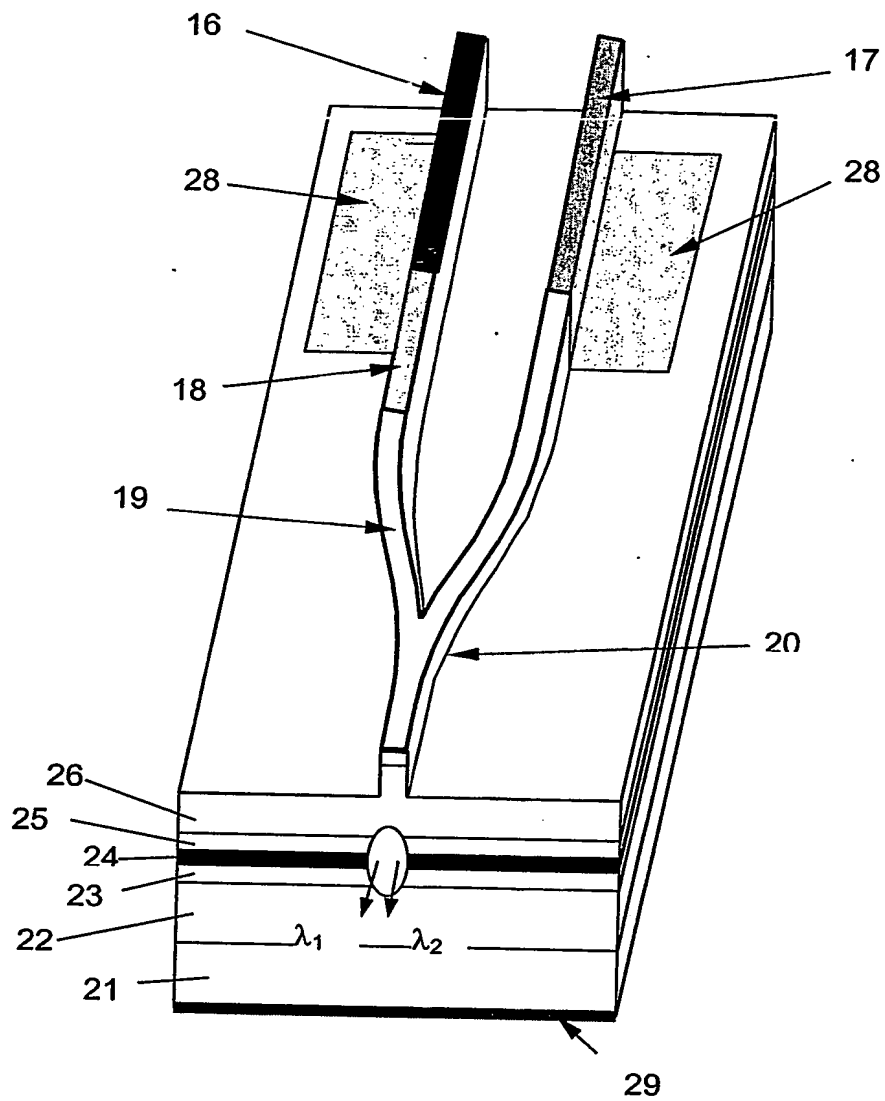


FIG. 11

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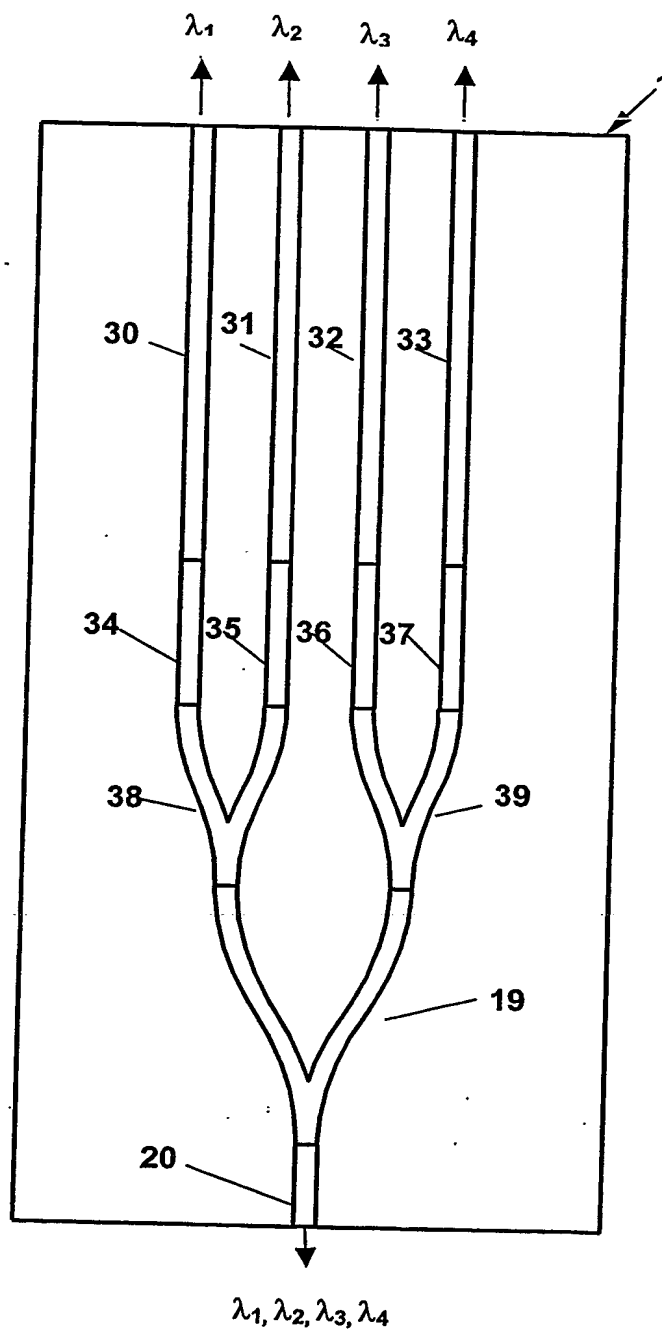


Fig. 12